EFFECT OF PLASTICIZER AND FERMETATION TIME ON CELLULOSE MEMBRANE PRODUCTION AND ANALYSIS OF MATERIAL PROPERTY

FARIDAH*, ALFIAN PUTRA, ELWINA, M. SAMI, NUR AZIZAH

Chemical Engineering Department, State of Polytechnic Lhokseumawe, Km 280 Buketrata Lhokseumawe, Lhokseumawe, 24301, Indonesia
**Email: ida4699@yahoo.com*

Abstract

This research has been carried out in cellulose membrane production from bacterial cellulose. Bacterial cellulose is produced from the fermentation process. The purpose of this study was to analysis the effect of cmc, glycerol and fermentation time towards cellulose membrane characteristics. Cellulose membrane made of a combination of coconut water and palm sugar juice as medium fermentation by using *Acetobacter xylinum* at 2, 4 and 6 days for fermentation time. Cellulose membrane obtained from a mixture of bacterial cellulose, cmc and glycerol. The addition of cmc and glycerol to improve cellulose membrane characteristics and performance. Based on the analysis results obtained the best performance at 4 days of fermentation time with a concentration of 1.5% cmc and 1.5% glycerol. The thickness of the cellulose membrane was almost the same for all samples and does not affect significantly towards the fermentation time for cellulose membrane production. Cellulose membrane has an asymmetric shape based on morphological analysis using SEM. Besides cellulose membrane has a similar pattern to the weight reduction and has the addition of heat resistance of the membrane. While the results of the IR spectra of cellulose membrane to detect the presence of OH groups, CO, C=C and CH groups that are characteristic of the polymer.

Keywords: Cellulose membrane; Plastizicer; Fermentation Time

Introduction

Bacterial cellulose is the result of the fermentation process using bacteria *Acetobacter xylinum* in a natural medium such as coconut water. It is known as *nata de coco*. The fermentation process produces a gel on the surface of the substrate sheet. It is also called bacterial cellulose[1]. Bacterial cellulose was known as a food ingredient. Besides as source of food, it can developed as functional materials in various industries such as the pharmaceutical industry[2], food industry[3], wound care productions[4], material constructions[5] and pulp and paper industry[6,7]. Bacterial cellulose produced in static culture when it can be futher processed into thin sheets which have unique properties including higher crystallinity degree, higher water retention ability, higher tensile strength and better mold ability[8,9].

To develop bacterial cellulose has done by previous researces, where bacterial cellulose can be applied as a cellulose membrane. Making cellulose membrane by using bacterial cellulose produced by modifying medium from coconut water and palm sugar juice. This study found that a ratio of 50% coconut water and 50% sugar palm juice has the good characteristic to produce cellulose membrane[10]. However, cellulose membranes are less elastic and easy fragile. Therefore, this study was conducted so that cellulose membrane can be elastic, not quickly torn and smooth. To make like that bacterial cellulose is needed to add some additives or plasticizer to make cellulose membrane to become elastic and smooth. Previous study found that the use of plasticizer such as glycerol and CMC can increase the elasticity and more flexible for bacterial cellulose. The addition of plasticizer aims to increase the mechanical properties of the polymer matrix. Plasticizer serves to be weakening style intermolecular bonding polymer. CMC and glycerol used as a material for the manufacture of membranes plasticizer. Indriyati[11] reported that studies have shown the addition of glycerol will reduce the mechanical strength of the polysaccharide. Glycerol proved to be effective to improve the properties of plastic films CMC. The addition of glycerol as a plasticizer to reduce the density and style between the substrate molecules (starch) with glycerol, so that the thin layer that forms a more flexible and smooth.

The purpose of this study was to determine the characteristics of cellulose membranes produced by the addition of glycerol and CMC on mechanical properties of cellulose membranes covering density, the thickness, the degree of crystallinity determine by x-ray diffraction (XRD), thermal decomposition behavior by TGA, scanning electron microscopy (SEM) for Determining the structure of the cellulose membrane, Universal

Tensile Machine for Determining tensile strength of cellulose membrane, and FTIR spectra of cellulose membrane.

Material and Methods

Culture Medium

Acetobacter xylinum culture obtained from Biotechnology laboratory of state Polytechnic lhokseumawe, Aceh, Indonesia. The cultures were incubated statically at room temperature in coconut water as culture medium. Three hundred mL of coconut water mixed with 8 g glucose, 2 g ammonium sulphate $(NH_4)_2SO_4$ and 0.5 mL glacial acetic acid (CH_3COOH). All media were sterilized at 121 ^oC for 15 min. This medium was boiled for 10 min. *Acetobcater xylinum* grown on this medium. *Acetobacter xylinum* was activated in coconut water and inoculated statically at room temperature around 30 ^oC for 7 days.

Bacterial Cellulose Production

All chemical were used to produce bacterial cellulose as nutrient. The culture medium was added some nutrients for bacterial cellulose production including sugar, acetic glacial, ammonium sulphate. The culture medium of bacterial cellulose production consists of 50% of coconut juice and 50% of sugar palm juice (*arenga pinnata* juice). Three hundreds of the mixture culture medium was added into 1 mL beaker glass and added 8 g of sugar, 2 g of ammonium sulphate, and 0.5 mL of acetic acid glacial and then stirring until homogeny. This medium was boiled and was cooled at room temperature. Starter of *Acetobacter xylinum* gently was added in culture medium and fermented at 2, 4 and 6 days in static batch to produce bacterial cellulose[12] and weighed.

Cellulose Membrane Production

Bacterial cellulose was washed with distilled water until the pH neutral and pre-treated with 2% NaOH for 24 hours. After soaking, the bacterial cellulose was neutralized with distilled water and were be pressed by hydraulic press to become film of cellulose membrane. Then, film of cellulose membrane boiled with distilled water for 10 minute. After that bacterial cellulose was boiled with water for ± 15 minutes and soaked for 24 hours. Bacterial cellulose was blended and soaked again for 24 hours. Then, It mixed with glycerol (% v/v): 0%, 1%, 1.5%, 2%, and 2.5% and CMC (% w/v): 0%., 1%, 1.5%, 2%, and 2.5% and heated for ± 15 minutes at 85^0C until homogeneous. The mixed material was printed on the glass plate and dried with oven at 100^0C. Cellulose membrane was produced.

Physical Properties of Cellulose Membrane

Thermogravimetric analysis (TGA)

The dynamic weight loss tests were determined on a thermo gravimetric analyser (TGA) machine (model Shimadzu DTG 60). For water content determination of cellulose membrane, all sample tests were conducted in a N_2 purge (40 ml/min) over a temperature range 30-650^oC at an increase rate of 10^oC/min. Cellulose membrane samples were placed on the absorbent wipers to eliminate excess water and thermal decomposition test, cellulose membrane samples were dried to 80^oC and analyzed then conducted in a N_2 purge (15 ml/min) over a temperature range 80-600^oC at an increase rate of 20^oC/min[13].

Microscopic of cellulose membrane with using SEM

Cellulose membrane was fixed and dehydrated on SEM merk JEOL JSM-651OLA . Cellulose membrane were cut with diamond and coated with gold. SEM JEOL JSM-651OLA field emission scanning electron microscope at 10 or 15 kV was used for sample examination. The picture were captured both top view and side view with 500x magnification[14].

FTIR of cellulose membrane

FTIR spectra were prepared on IR-Prestige-21 Shimadzu spectrometer. The samples could be analysed without dilution and samples spectra were acquired in rapid scan mode with a 1 kHz modulation frequency and by averaging scan at 4 cm^{-1} resolution.

Results and Discussion

The Quality and Thickness of Cellulose Membrane

This research has produced a cellulose membrane. Cellulose membranes were produced from a mixture of bacterial cellulose, glycerol and CMC. From the results were obtained that the cellulose membrane from the addition of glycerol to be more soft and flexible than the cellulose membrane from control without glycerol addition. This is because the addition of glycerol to reduce the density and inter-molecular force between bacterial cellolose and glycerol, so that cellulose membrane formed more flexible[15]. But the addition of glycerol more than 1% conduced cellulose membranes softer and sticky after drying in an oven at 100 ^{o}C. It is also found by Lucia, where the addition of 1.5% glycerol produce bacterial cellulose composite layer is soft and sticky. Cellulose membrane production is soft and sticky because glycerol influenced by binding water and soften the surface[11,15]. While the addition of the CMC cellulose membranes produce more hard and brittle. Because CMC has hydroxyl groups that are forming intermolecular hydrogen bonds formed between a thin layers consisting of fibers that reinforce each other[16].

Table 1. Average thckness of cellulose membrane

Fermentation Time	Glycerol and CMC Concentration	Cellulose Membrane Thinkness (mm)		
(day)	(%)	CMC	Glycerol	CMC and Glycerol
	0	0,012	0,012	0,012
	1	0,012	0,012	0,011
2	1,5	0,015	0,012	0,017
	2	0,012	0,012	0,015
	2,5	0,011	0,015	0,011
	0	0,015	0,011	0,011
	1	0,012	0,012	0,011
4	1,5	0,012	0,015	0,015
	2	0,015	0,012	0,011
	2,5	0,011	0,015	0,015
	0	0,017	0,017	0,017
	1	0,017	0,017	0,012
6	1,5	0,015	0,015	0,012
	2	0,012	0,012	0,015
	2,5	0,012	0,012	0,015

Preparation of cellulose membrane with a casting method produces thin sheets with uniform thickness and homogeneous. In Table 1, it can be seen that the thickness of the cellulose membrane produced nearly the same for all variables. The addition of glycerol and CMC does not affect the thickness of the cellulose membrane. It also does not affect the fermentation time from bacterian cellulose production towards the thickness of cellulose membrane. Due to the cellulose membranes were produced from bacterial cellulose in the form of slurry, so that the time in generating fermentation of bacterial cellulose did not affect the thickness of cellulose membrane.

Cellulose Membrane Structure and Physical Properties

a. Thermogravimetric Analysis (TGA)

In this study, thermal decomposition of cellulose membrane have been analyzed by TGA equitment. Thermal decomposition behaviour of cellulose membrane samples can be described in fig. 1. It shows that the thermal stability of cellulose membrane from different cellulose membrane samples. This cellulose membrane was produced from the addition of 1.5% cmc, 1.5% glycerol and bacterial cellulose which produced from fermentation time at 4 days. The thermal stability for cellulose membrane samples were found that their pattern for thermal stability have the same pattern. Whereas fig. 1 consists of two steps for weight loss of cellulose membrane, it indicated the possibility of two types of decomposition[7]. The weight loss at lower temperature ranging from 300^{o}C to 360 ^{o}C has the same pattern which illustrated Chen from 200^{o}C to 360 ^{o}C[7]. From this figure 1, it desribes that cellulose membrane with the addition of glycerol have the lower persent weight that the others. It was indicated the release of water and the removal of small molecular fragments such as hydroxyl and methyl hydroxyl groups[17]. The second weight loss ranging from 360^{o}C to 600^{o}C showed the degradation of

polymeric chains[7]. Thermal stability of cellulose membrane is affected by some structure parameters of this cellulose membrane.

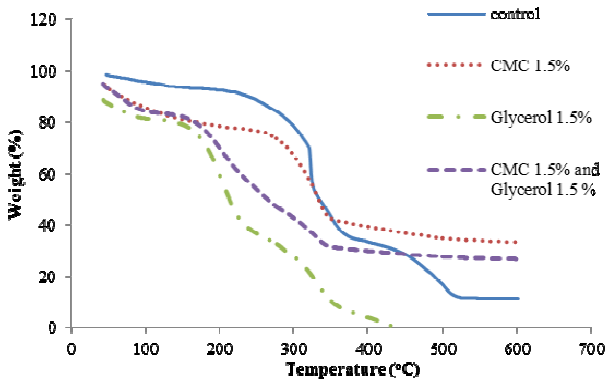
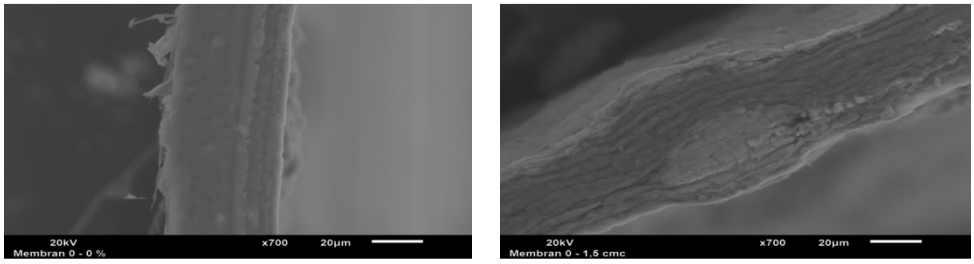


Fig.1 Thermal stability of cellulose membrane from fermentation time at 4 days

b. Scanning Electron Miscroscopic (SEM)

Scanning electron miscroscopic (SEM) was analyzed for cellulose membrane. The surface of cellulose membranes made with magnification 700 times. The results were obtained for both cellulose membranes. The structure of cellulose membrane is sufficiently tight and it is shown in fig. 2a. The more tightly Structure-cellulose membrane made solvent molecule diffusion so hard to produce a smaller pore size[18]. While the structure of cellulose in fig. 2b. has shaped grooves, very tight and porous layers as a spinger. That pores are not homogeneous (asymmetric) and suitable for ultrafiltration membranes. The tightly pore structure stating that the morphology of the membrane surface is not homogeneous and a tight layer formed after interfacial polymerization process.



(a) (b)

Fig. 2 Scanning Electron Miscroscopic of cellulose membrane from fermentation time at 4 days (a) cellulose membrane without cmc addition (control); (b) cellulose membrane with 1.5% cmc addition

c. FTIR of Cellulose Membrane

Analysis of cellulose membrane using FTIR aims to find solvents or additives that are bound or trapped in the membrane. A new bond between the cellulosa membrane with solvents and additives, it will change the absorption peaks of the IR spectrum.

Cellulose membranes for all samples have the same pattern, it shows in fig. 3. It explains that the addition of cmc and glycerol in the manufacture of cellulose membrane did not change for group functions. However, the intensity is very different for all samples. FTIR spectra was found some peaks that describe the chain of cellulose. Characteristic absorption peak of bacterial cellulose is an OH group occurs at wave number 3284.56 cm^{-1} and the CO group at wave number 1062.87 cm^{-1}. It was illustrated by Lindu, M[18]. FTIR analysis of all samples of cellulose membranes indicated that they have the same pattern. The absorption intensity at 3356,44 cm^{-1}, which described a OH functional group, was found for all samples. It also was described CO group stretching at 1062.78 cm^{-1} absorption. There are also other groups such as C=C group at 2133.27 cm^{-1} and 1635.64 cm^{-1} in absorption area while the CH on the absorption area around 2733.13 cm^{-1} and 2914.44 cm^{-1}.

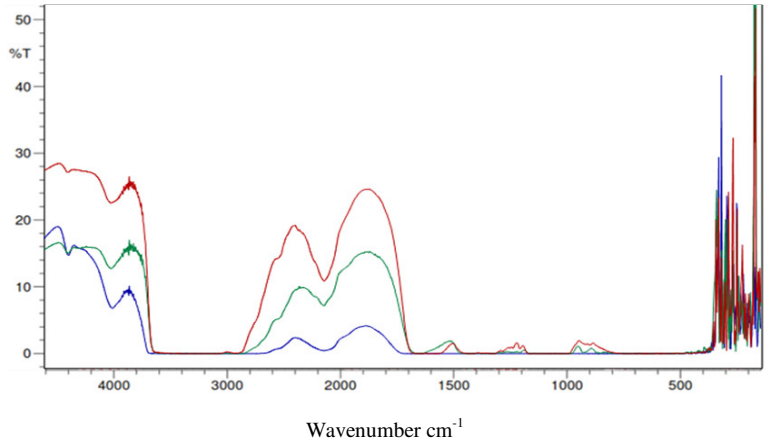


Fig. 3 FTIR spectra of cellulose membrane from fermentation time at 4 days with plasticizer addition; line red colour for 1.5% CMC; line green colour for 1.5% glycerol; line blue colour for cmc and glycerol was mixed

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